

Temperature Dependence of the Index of Refraction of Fused Silica

Answer to Question # 50

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Because the coefficient of thermal expansion of fused silica¹ is so small ($\approx 0.4 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$ at room temperature), it is evident that the variation in refractive index² ($dn/dT \approx 1.1 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$) must result from a change in the internal structure of the material with temperature. Note, also, that dilution of dispersive material by thermal expansion would tend to produce a negative dn/dT , opposite to what is observed. Here we develop the most elementary possible model. It is qualitatively, but not quantitatively, consistent with the data.

We write the complex dielectric constant $\epsilon(\omega)$ as the sum of real and imaginary parts

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega), \quad (1)$$

with $\epsilon'(\omega)$ and $\epsilon''(\omega)$ each real. Then we use one of the Kramers-Kronig relations³

$$\epsilon'(\omega) = 1 + \frac{2}{\pi} \text{P} \int_0^\infty \frac{s\epsilon''(s)}{s^2 - \omega^2} ds. \quad (2)$$

We assume that $\epsilon''(\omega)$ is narrowly peaked near a high (ultraviolet) frequency $s_0 \gg \omega$.

At zero temperature $\epsilon''(\omega)$ may be a Dirac δ -function, or a sum of δ -functions, each corresponding to an allowed vibronic transition, or to its analogue in an amorphous solid. At finite temperature T the excited vibrational (phonon) substates of the ground electronic state are excited. In general, these have the same allowed transitions to excited electronic states as the vibrational ground state, and we will assume they have the same oscillator strengths. Assuming a classical distribution of ground state vibrational excitation (requiring, in a crystal, a temperature in excess of the Debye temperature) yields a simple

analytical model for $\epsilon''(\omega)$:

$$\epsilon''(s) = \begin{cases} \frac{C\hbar}{k_B T} \exp[\hbar(s - s_0)/k_B T] & s < s_0 \\ 0 & s \geq s_0, \end{cases} \quad (3)$$

where C is a normalization constant. This model assumes a single allowed electronic transition of (zero-temperature) frequency s_0 , but may be applied if there are many such transitions, each with a frequency $\gg \omega$, if s_0 is taken as an oscillator strength-weighted average. It tacitly neglects any temperature dependence of the Franck-Condon factors.

Using (3) in (2) yields

$$\epsilon'(\omega) = 1 + \frac{2}{\pi} \text{P} \int_0^{s_0} \frac{s}{s^2 - \omega^2} \frac{C\hbar}{k_B T} \exp[\hbar(s - s_0)/k_B T] ds \quad (4)$$

If we approximate $k_B T \ll \hbar s_0$ then the integrand is narrowly peaked around $s = s_0$. The lower limit of the integral may be extended to $-\infty$ and $s/(s^2 - \omega^2)$ expanded in a Taylor series about s_0 :

$$\frac{s}{s^2 - \omega^2} = \frac{1}{s_0} - \frac{(s - s_0)}{s_0^2} + \frac{1}{2} \frac{4\omega^2}{s_0^5} (s - s_0)^2 - \dots \quad (5)$$

This removes the pole in the integrand. Then the integral is elementary, yielding

$$\epsilon'(\omega) - 1 = \frac{2}{\pi} \frac{C}{s_0}, \quad (6)$$

which determines C .

Differentiating (4) yields

$$\frac{d\epsilon'(\omega)}{dT} = -\frac{2}{\pi} \int_0^{s_0} \frac{s}{s^2 - \omega^2} \frac{C\hbar}{k_B T} \left(\frac{\hbar(s - s_0)}{k_B T} + 1 \right) \exp[\hbar(s - s_0)/k_B T] ds. \quad (7)$$

Again taking $k_B T \ll \hbar s_0$ and $\omega \ll s_0$, the first term in the expansion (5) integrates to zero but the second yields the result

$$\frac{d\epsilon'(\omega)}{dT} = \frac{2}{\pi} \frac{C k_B}{\hbar s_0^2} = [\epsilon'(\omega) - 1] \frac{k_B}{\hbar s_0}. \quad (8)$$

In terms of the refractive index $n = (\epsilon\mu)^{1/2} = \epsilon^{1/2}$

$$\frac{dn(\omega)}{dT} = \frac{n^2 - 1}{2n} \frac{k_B}{\hbar s_0}. \quad (9)$$

In order to evaluate this numerically we need to estimate s_0 . Fused silica has very strong ultraviolet absorption centered around a wavelength of 1200 \AA , implying $\hbar s_0 \approx 1.6 \times 10^{-11} \text{ erg}$. Then, with $n = 1.445$ in the visible and near-infrared, we have

$$\frac{dn}{dT} = 3.2 \times 10^{-6} \text{ }^\circ\text{K}^{-1}. \quad (10)$$

This theoretical value is about 3.4 times less than the measured² value of $1.1 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$. The most plausible explanation of the discrepancy is that the Franck-Condon factors are increasing functions of temperature, as increasing vibrational excitation of the electronic ground state increases the range of internuclear separations, providing a better match to upper states in which the equilibrium internuclear separation is greater. This effect cannot be calculated analytically.

The theory predicts that dn/dT be nearly independent of frequency because n is nearly independent of frequency. This is observed² to be true to within about 10% for wavelengths between 3000 \AA and 4μ . dn/dT is measured to increase with decreasing wavelength for $\lambda < 3000 \text{ \AA}$, where the assumption $\omega \ll s_0$ is no longer valid. The theory could readily be extended to these larger values of ω by means of a straightforward numerical integration.

¹ American Institute of Physics *American Institute of Physics Handbook* (McGraw-Hill, New York, 1957).

² I. H. Malitson, "Interspecimen Comparison of the Refractive Index of Fused Silica," J. Opt. Soc. Am. **55**, 1205–1209 (1965).

³ J. D. Jackson *Classical Electrodynamics* (Wiley, New York, 1962), Prob. 7.9.